JACS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
COMMUNICATION
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A Robust, Air-Stable, Reusable Ruthenium Catalyst for Dehydrogenation of Ammonia Borane

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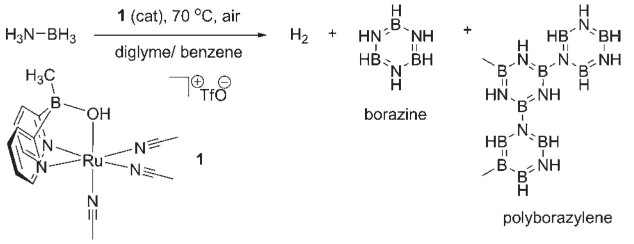
Ⓢ *Supporting Information*

ABSTRACT: We describe an efficient homogeneous ruthenium catalyst for the dehydrogenation of ammonia borane (AB). This catalyst liberates more than 2 equiv of H_2 and up to 4.6 system wt % H_2 from concentrated AB suspensions under air. Importantly, this catalyst is robust, delivering several cycles of dehydrogenation at high [AB] without loss of catalytic activity, even with exposure to air and water.

Catalytic dehydrogenation of ammonia borane (AB) is an active research area because AB is a potentially useful hydrogen storage medium for transportation.[1] This is because of its high hydrogen density (19.6 wt %), ability to release H_2 under mild conditions (both thermal[2] and catalytic), and its desirable physical properties. Though catalytic hydrolysis is well-known and very efficient for H_2 production from AB,[1b] anhydrous dehydrogenation can enable a more efficient fuel cycle. This is because hydrolysis reactions form stoichiometric quantities of ammonia, a hydrogen fuel cell poison, and strong B−O bonds, which preclude an efficient regeneration scheme.[3] Several heterogeneous[4] and homogeneous[5] transition-metal catalysts are active for AB dehydrogenation, but these are limited by protic and oxidative decomposition in air, low extent of H_2 release (≤2 equiv), uncontrolled rate of H_2 release, or production of unwanted products such as ammonia (NH_3) or borazine ($N_3B_3H_6$), which are poisonous to fuel cells. Additionally, many are not viable because the catalyst loading is high or the catalyst is not reusable. We report here a system that is long-lived [turnover number (TON) > 5000], functions under air, and dehydrogenates AB to give >2 equiv of H_2. These characteristics make it a leading candidate for use in a commercial H_2 storage system.

Scheme 1. Dehydrogenation of Ammonia Borane to Produce Hydrogen, Borazine, and Polyborazylene



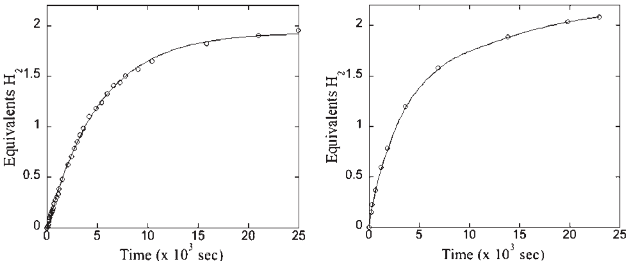


Figure 1. (left) H_2 production from AB with 5.0 mol % **1** under air at 70 °C in 11:1 diglyme/benzene solution. (right) H_2 production from AB in the presence of 2.0 mol % **1** in tetraglyme under air at 70 °C at high [AB]. H_2 release = 4.2 system wt %.

Catalyst **1**[6] liberates H_2 from AB under air in diglyme solutions (Scheme 1). To determine the efficiency of AB dehydrogenation with **1**, we treated a 0.42 M AB solution with 5.0 mol % **1** at 70 °C in a Schlenk flask under air and monitored the production of H_2 using a eudiometer. The system produced 1.94 equiv of H_2 in 7 h (Figure 1 left). Added metallic mercury did not inhibit the reaction under these conditions, which indicates homogeneous catalysis.[7] We also examined more practical, highly concentrated suspension conditions. A slurry of AB and tetraglyme (100.0 mg of AB, 202.6 mg of tetraglyme, 5.8 system wt % stored H_2) was treated with 2.0 mol % **1** at 70 °C and yielded 2.0 equiv of H_2 in 4 h and a total of 2.2 equiv (TON = 110) upon completion of the reaction. This corresponds to the release of 4.2 wt % H_2. In contrast, uncatalyzed AB dehydrogenation[8] liberates only 1.6 equiv of H_2 at 70 °C at a rate that is ca. 2.5-fold slower under our reaction conditions (see the Supporting Information).

This catalyst system is also remarkably reusable. Data for successive runs at 2.0 mol % loading (70 °C) indicate that the catalysis is efficient through four ca. 6 h runs at high [AB], although the reaction slurry becomes viscous. To help alleviate this situation, we added 0.2 mL of tetraglyme while recharging the reactor with AB for subsequent runs. In this way, we ran four successive runs in a single reactor. The rates for all of these were similar, and they released 2.2, 2.1, 2.3, and 2.2 equiv of H_2, respectively, for a total TON of 440. With a catalyst loading of 0.1 mol %, we observed a TON of ca. 5700 over three runs and liberation of up to 4.6 wt % H_2.[9] For comparison, Fagnou reported a ruthenium catalyst that could release up to 1.0 system wt % H_2 from AB at room temperature and up to 3.6 system wt %

Received: June 26, 2011
Published: August 09, 2011

H_2 from AB/$MeNH_2BH_3$ mixtures at 50 °C.[5b] This is the best previously published weight-content H_2 release for a homogeneous catalytic system dehydrogenating an amineborane.

Our system works well when open to air, which is beneficial for commercialization: a system stable to air and water provides practical advantages over a more sensitive one. Measurement of H_2 produced in eudiometry studies in air and under N_2 were identical under concentrated AB conditions. To quantify this effect further, we compared rate constants (k_{obs}) for [AB] consumption obtained for reactions conducted under nitrogen and air. In this experiment, 2.5 mol % **1** was prepared in diglyme/benzene-d_6 in a glovebox and sonicated open to air for 1 h prior to addition of AB to ensure removal of the N_2 environment and establish atmospheric O_2 levels in the NMR tube. The k_{obs} values at 70 °C were $2.65(9) \times 10^{-4}$ s^{-1} in air and $2.54(9) \times 10^{-4}$ s^{-1} in N_2. Thus, we observed neither inhibition nor acceleration of the catalysis. This suggests that at ambient levels of O_2, the catalysis is not shut down by decomposition of the active species or accelerated by formation of a more reactive, higher-valent ruthenium oxo complex.

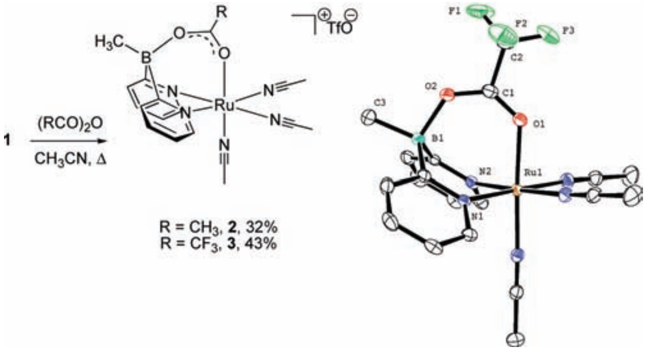
We probed the mechanism of AB dehydrogenation with **1** by ^{11}B NMR spectroscopy in dilute diglyme solutions. Unlike Shvo's catalyst,[5e] **1** demonstrates first-order kinetics in [AB] through 3 half-lives, as observed by the disappearance of the AB resonance in the ^{11}B NMR spectrum. Similar to others' observations, the intermediates we observed in these reactions are branched and unbranched cyclotriborazane, aminoborane oligomers, borazine, and polyborazylene (PB),[1a,1d,8] with the latter two being the major products upon completion. As is the case for Shvo's catalyst,[5e] we did not observe the formation of insoluble B,N oligomers in this system.

The appearance of PB at early times in reactions with **1** is encouraging, whereas none is seen under Shvo conditions. Formation of PB is a feature of extensive dehydrogenation, indicating the production of more than 2 equiv of H_2, and it has been proposed to occur by borazine cross-linking in transition-metal-catalyzed systems. However, in contrast to (NHC)Ni systems, in which borazine is quickly consumed,[5d] [borazine] increases over time in reactions of **1** and is not consumed late in the reaction.[10] This suggests that catalytic borazine cross-linking is not the mechanism for PB formation in this system. We suspect that the operative mechanism involves reaction of borazine with AB or one of its early dehydrogenation products. Efficient, catalytic borazine cross-linking has not been demonstrated to date in the absence of other B,N materials.[11]

Rate data (k_{obs}, 70 °C) collected by ^{11}B NMR spectroscopy were pseudo-first-order in AB. A catalyst order study was conducted by comparing the k_{obs} values measured at various concentrations of **1**. The data gave a linear plot of $\ln(k_{obs})$ versus $\ln([\mathbf{1}])$ with a slope of 0.56, which indicates the presence of a dinuclear $(Ru)_2$ intermediate,[12] although we did not observe this species. Possible structures include those containing a B—O—B bridge, a bridging hydride, or a product of AB dehydrogenation serving as the bridging moiety. Along these lines, we did not observe a persistent metal hydride, which argues against a Ru—H moiety as the resting state of the catalyst. This is in line with observations of the (NHC)Ni systems[5d] but contrasts our own[5e] and others' findings for ruthenium[7] and iridium[5a] catalysts.

We suspect that **1** might be analogous to several known catalysts that interact with the polarized B—H and N—H bonds of AB concurrently in a bifunctional transition state.[5b,5f,13] We probed this by recording deuterium isotope effects for isotopologues of AB.[14] The k_H/k_D values for the B—H and N—H bonds were 1.22(14) and 1.58(9), respectively. A combined isotope effect measured using D_3N-BD_3 (k_{NHBH}/k_{NDBD}) was 1.67(18). Thus, the product of the two independently measured isotope effects [1.92(25)] is within experimental error of the measured double isotope effect, which is consistent with a concerted, asynchronous transition state in the rate-determining step. However, this conclusion is tentative because we cannot be certain whether the observed isotope effects involve H_2 transfer from AB to the catalyst or multiple steps, as in the (NHC)Ni system.[13a]

Scheme 2. Synthesis of Bridging Carboxylate Complexes 2 and 3[a]



[a] (left) Synthesis. (right) ORTEP plot of **3** with 50% probability ellipsoids. H atoms and the triflate counterion have been omitted for clarity.

Other mechanistic scenarios have the bridging hydroxyl group of **1** donating H^+ to the solution, thus initiating an acid-catalyzed reaction,[15] or the thus-formed oxide bridge providing an internal base in a bifunctional mechanism. To probe these, we synthesized bridging carboxylate complexes **2** and **3** (Scheme 2 left), which are devoid of the protic functionality. The crystal structure of **3** (Scheme 2 right)[16] shows an unprecedented Ru—B μ_2-κO:$\kappa O'$ bonding mode for the trifluoroacetate wherein the boron is distorted from its tetrahedral geometry to give a trigonal-pyramidal structure. This behavior could be rationalized by unfavorable steric interactions between the bridging carboxylate and other ligands in the unobserved μ_2-κO:κO (single bridging oxygen) mode. We suspect the same for **2**.

Surprisingly, 5.0 mol % solutions of **1** and **2** have the same rate constant for AB consumption [$k_{obs} = 3.74(7) \times 10^{-4}$ and $3.72(10) \times 10^{-4}$ s^{-1}, respectively, at 70 °C]. This disfavors a H^+-catalyzed mechanism. To interrogate the potential role of boron as a Lewis acid, we attempted AB dehydrogenation with complex **3**, which has different electronic characteristics than **1** or **2**. This gives faster catalysis: 2.5 mol % solutions of **1** and **3** gave rate constants of $k_{obs} = 2.66(12) \times 10^{-4}$ and $5.77(12) \times 10^{-4}$ s^{-1}, respectively, for AB consumption at 70 °C. Thus, the occupancy of the bridging coordination site between Ru and B has an important influence on the dehydrogenation rate.

In multiple solvents we observed that the acetate and trifluoroacetate complexes hydrolyze completely in the presence of trace water to re-form bridging hydroxide complex **1** and the corresponding carboxylic acid, which indicates a thermodynamic preference for the Ru(OH)B bridge. Adding water (ca. 6 equiv) to a sample of **3** in tetrahydrofuran-d_8 reveals that the hydrolysis has a half-life of 6−7 h at room temperature, thus demonstrating the lability of the carboxylate ligand. Furthermore, a methylene chloride-d_2 solution of **3** and 1 equiv of TFA-d_1 showed the coalescence of the bound and free trifluoroacetic acid (TFA) signals at 50 °C as monitored by ^{19}F NMR spectroscopy: two fluorine resonances [δ −75.38 (bound) and −75.25 (free) at 25 °C] coalesced to one (δ −75.51). This observation indicates that exchange occurs rapidly on the NMR time scale. Thus, the bridging trifluoroacetate appears to be sufficiently labile to allow boron and ruthenium to participate in catalysis, but these data do not rule out participation of the acetate and trifluoroacetate in the mechanism of AB dehydrogenation by **2** and **3**, as has been documented in systems for hydrocarbon C−H activation.[17]

Importantly, dehydrogenation is not efficient in the absence of the borate ligand. Catalyst **1**'s nonligated synthetic precursor, $[(\text{cym})\text{RuCl}_2]_2$ (**4**), does not participate in efficient catalysis; these reactions precipitate metallic material under our experimental conditions. ^{11}B NMR data for catalysis with **4** revealed a rate of AB consumption that is only ca. 2-fold lower than that of **1**; however, H_2 production from this system was limited to 1 equiv, and it is not reusable. Additionally, added metallic mercury significantly attenuated the production of H_2 with **4**. Full kinetics data for AB dehydrogenation with **4**, $\text{Na}[(2\text{-py})_2\text{BMe}_2]$, and $[((2\text{-py})_2\text{BMe}_2)\text{RuCl}(\text{cym})]$ (**5**) are described in the Supporting Information.

In conclusion, we have demonstrated an efficient and robust catalyst for highly productive ammonia borane dehydrogenation. This catalyst liberates up to 4.6 wt % H_2 from AB suspensions and is resistant to deactivation in air, which makes it one of the most appealing homogeneous transition-metal catalysts designed to date. Its longevity at low catalyst loadings (TON up to 5700) and its air stability are unprecedented in transition-metal-catalyzed AB dehydrogenation. Initial mechanistic investigations based on (1) isotope effects and (2) the relative reaction rates of **2** and **3** suggest that dual-site cooperativity could be operative. This mechanistic insight may lead to the development of more efficient systems for AB dehydrogenation. Ongoing work in our laboratory involves uncovering the detailed roles of the boron and ruthenium centers in AB dehydrogenation and the application of dual-site catalysis to more general hydride manipulation reactions.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Full experimental procedures, characterization of complexes **2** and **3**, full kinetics data for AB dehydrogenation with **1**−**5** and $\text{Na}[(2\text{-py})_2\text{BMe}_2]$, a comment on the [EtOH] dependence of the rate, and crystallographic data (CIF) for **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENT

We thank the National Science Foundation (CHE-1054910), the University of Southern California, the Loker Hydrocarbon Research Institute, and the Hydrocarbon Research Foundation for research support and the NSF (DBI-0821671, CHE-0840366) and NIH (S10-RR25432) for NMR spectrometers. We thank Ralf Haiges for the X-ray study of **3**.

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